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AOARD REPORT

Diamond and Functionally Gradient Materials, Japan

May 16-29, 1993
J. Chin
Consultant

This report provides a summaries of trips in May, 1993 by Jack Chin and Shiro Fujishiro to assess the status of New Diamond and Functionally Gradient Materials Technology in Japan

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TRIP REPORT, MAY 16-29, 1993

(Jack Chin and Shiro Fujishiro)

TRIP PURPOSE: To assess the status of New Diamond and Functionally Gradient Materials Technology in Japan

DESTINATIONS: Attendance at the 183rd Meeting of The Electrochemical Society for the most current international progress in New Diamond research.

Visits to Select Japanese Universities, Government Research Centers and Private Research Laboratories Engaged in Functionally Gradient Materials or Vapor Deposited Diamond Research.

The 183rd Meeting of the Electrochemical Society May 16-21, 1993

(Attended by Jack Chin)

Over 2100 papers were presented at the 183rd meeting of The Electrochemical Society, held in Honolulu, May 16-21, 1993. The meeting was cosponsored by the Electrochemical Society of Japan with the cooperation of The Japan Society of Applied Physics. The Third International Symposium on Diamond Materials and the Twelfth International Conference on Chemical Vapor Deposition (CVD XII) were part of this meeting. In both these conferences, recent research studies on vapor deposited diamond in Japan, were reported. Thirty five papers from the Diamond Symposium and twenty one papers from the CVD Conference were heard.

Session topics for the Diamond Symposium were:

A. Theory, Modeling, Gas Phase Chemistry
B. Nucleation and Growth
C. Deposition Techniques

D. Applications
E. Characterization
F. Fabrication, Processing, Economics
G. Applications- Electronics and Tribology

Session topics for the CVD Conference were:

A. Compound Semiconductors
B. Fundamentals
C. CVD Models and Technology
D. Si and Si/Ge Epitaxy
E. Conductors
F. Dielectrics
G. Coatings and CVI

The level of international interest and research effort in New Diamond technology has increased dramatically in the last 2 years. The principal contributors were from United States, Japan, Russia and Germany. Nine other countries presented 24 papers to this diamond symposium. The number of papers from Japan, while second in number to those from the United States, were fewer than expected. This was thought to be partially due to an upcoming Applied Diamond Conference to be held in Omiya, Saitama Japan, August 25-27, 1993.

Contact was made at the conference, with several Japanese presenters whom I would not be able to visit in Japan. I wanted to include their work in our technical assessment of diamond and FGM technology. Those who were professors or senior persons in their organizations talked openly with me about papers presented in Honolulu but invited me to visit them rather than have discussions in Honolulu about other work they were doing. One subordinate presenter became very nervous when I talked to him. He said even the perception of a technical discussion with me or any foreigner without a formal, prior approved agenda, was career threatening. He would not even discuss the paper he had just presented. He said he could not discuss details because his work was government sponsored and thus had severe restrictions on information transfer to foreign nationals. He implored me not to include his name in any trip report and moved away as fast as he could. His reaction was not surprising since he was not a group leader and the wrong independent action on his part would ruin him. His comments did reinforce the concept that the best way to maximize our understanding of Japanese technology is by cultivating direct contact interface meetings with technology leaders through site visits, symposiums, workshops, and cooperative research programs.

VISITED ASSESSMENT SITES IN JAPAN

(By Shiro Fujishiro and Jack Chin)

The tables that follow contain information about assessment sites visited from May 24-28, 1993. A mix of government, private companies, and universities were selected. The senior person in each of these organizations has an international reputation for excellence in his field of study. Dr. Niino, at the National Aerospace Laboratory, one of the pioneers of Japanese functionally gradient materials (FGM), is credited with being the principle planner of the current National Japanese program on functionally gradient materials. Professor Watanabe of Tohoku University is one of the pioneers of Japanese gradient materials research. Dr Fujioka and his staff at Kawasaki Heavy Industries' Material Research Department are commercializing FGM technology.

Professor Hirai of Tohoku has been publishing chemical vapor deposition (CVD) research papers internationally for over 25 years. He is not only current in recent advances in CVD processes but his group is actively engaged in research on functionally graded materials, nano-composites and diamond. Professor Hiraki and his staff of the department of Electrical Engineering at Osaka University are involved in a wide spectrum of diamond research projects. He also organizes vapor deposited diamond and semiconductor conferences and workshops in Japan and internationally. Professor Inuzuka of Aoyama Gakuin University is one of the pioneers of Japanese New Diamond research. Dr. Nogi of the Welding Institute is a specialist in surface studies. His concerns are metal-metal, ceramic-ceramic, and ceramic-metal joining. As part of this effort he is developing solutions to diamond-substrate interface problems needed in CVD diamond development. Dr. Shohata of NEC Materials Research and Naoji Fujimori of the Electronics Materials R&D Department of Sumitomo Electric Industries have both been successful in finding new applications for CVD Diamond technology to real world material problems.

Assessment Sites in Japan

Functional Graded (FGM) Materials

Scientists	Interest	Organization	Location
T. Hirai, M. Omori	FGM, Nano-Composites, CVD, PECVD, ECR-PECVD Superconductors, CVI	Institute For Materials Research Tohoku University	Katahira, Aoba-Ku, Sendai 980
R. Watanabe	FGM with active cooling, SiC-AlN, Ceramic Powders, SiC-AlN/Mo	Dept. Materials Processing, Tohoku University	Sendai, 980
M. Niino, A. Kumakawa, L. Chen, Y. Kuroda, T. Saito	FGM with active cooling, C/C Spaceplane Combustors	Kakuda Research Center National Aerospace Laboratory,	Koganezawa 1, Kimigaya, Kakuda City Miyagi 981-15
J. Fujioka, Y. Matsuzaki, S. Tanaka, T. Suemitsu, K. Hasegawa, M. Kawamura	C/C Spaceplane Combustors, SS/FGM-ZrO_2/SS	Akashi Technical Institute, Kawasaki Heavy Industries, Ltd.	1-1, Kawasaki-cho, Akashi 673, Japan

Vapor Deposited Diamond

Scientists	Interest	Organization	Location
A. Hiraki, A. Hatta,	Magneto-Active PECVD, Low Temp. Diamond Semiconductors	Department of Electrical Engineering, Osaka University	2-1, Yamadaoka, Suita-shi Osaka 565
N. Fujimori	Speaker Domes Heat Sinks FET	Itami Research Laboratories, Sumitomo Electric Ind.	1-1-1, Koya-kita, Itami, 664
N. Shohata, K. Baba	Electronics, Optical Windows, X-ray Masks	NEC Corp., Materials Research Laboratory	Miyamae-ku, Kawasaki, Kanagawa 216
T. Inuzuka	Fundamentals of Diamond Growth, Heteroepitaxial Diamond	Aoyama Gakuin University, Electrical Engineering and Electronics	Setagaya-ku Chitosedai 6-16-1 Tokyo 157
K. Nogi	Diamond Nucleation, Joining Ceram./Ceram., Metal/metal, Wetability	Welding Research Institute	11-1 Mihogaoka Ibaraki, Osaka, 567

The hosts at all the visited sites were cordial and cooperative. Some university groups were very open about the projects they were working on, the number of people assigned to these projects and their future plans. They welcomed and encouraged visits to their laboratories. Others organizations were reluctant about discussing anything with us that had not already been made public through written reports or internally approved advertisements. Access to their laboratories was limited or not invited. The private companies were understandably the most restricted with information they would give us. They were even careful about providing any data from which we might be able to estimate the level of their research efforts.

Observations and comments about the technical activities at each site are given in the technology assessment report. However a few comments are perhaps best noted here. The national FGM program is a well planned, long termed effort with focused objectives. Those organizations involved in this effort have adequate funding to install sophisticated, expensive, hardware needed to produce and characterize these materials. Japan is currently the world leader in FGM research. It is our impression that there is no current Japanese national agenda for New Diamond research that is comparable to the Japanese FGM program. The difference may be due to a lack of specifically targeted applications for diamond technology in government planned projects. In spite of this apparent limited national funding, the universities and private companies are continuing to sponsor New Diamond development which keeps Japan as one of the world leaders in this technology.

June 10, 1993

ASSESSMENT OF FUNCTIONALLY GRADIENT MATERIALS AND VAPOR DEPOSITED DIAMOND TECHNOLOGY IN JAPAN

Jack Chin and Shiro Fujishiro

July 30, 1993

1. ASSESSMENT SUMMARY

1.1 Overview

An assessment was made of Japanese research activities in Functionally Gradient Materials (FGM) and vapor deposited diamond technologies. Attempts were made to evaluate current research projects, long range technology goals, government-university-industry cooperative programs, and trends in commercialization of these technologies. The basis for these assessments were largely the results of visits to selected sites where these technologies are being developed. The sites selected for these visits included government, university and industrial research laboratories. The hosts at all the visited sites were cordial and cooperative. Some university groups were very open about their research projects, the number of people assigned to these projects and their future plans. They welcomed and encouraged visits to their laboratories. Others organizations were reluctant to discuss anything with us that had not already been made public through written reports or internally approved advertisements. Access to their laboratories was limited or not invited. The private companies were understandably the most restricted with information they could give us. Some organizations were even careful about providing any information from which we might be able to estimate the level of their research efforts.

The original focus of Japanese FGM research was the application of FGM technology to solve materials problems associated with the national aerospace plane. This work ended but a new national effort on FGM for space power has begun. Japan is currently the world leader in FGM research. The national FGM program is a well planned, long termed effort with focused objectives. Those organizations involved in this national FGM research effort have adequate funding to install sophisticated, expensive, hardware needed to produce and characterize these materials.

It is our impression that there is no current Japanese national agenda for Vapor Deposited Diamond research that is comparable to the national FGM program. The difference may be due to a lack of specifically targeted applications for diamond technology in government planned projects. In spite of this apparent limited national funding, the universities and private companies are continuing to sponsor Vapor Deposited Diamond development which still keeps Japan as one of the world leaders in this technology.

1.2 The Japanese Approach

The Japanese approach to technology development is clearly demonstrated in the progress that has been made in both functionally graded materials and vapor deposited diamond developments. What is different about this Japanese approach from the American approach is strong group interaction between diverse organizations within the designated groups of material designers, process developers, testing and application engineers. Even small projects show joint efforts by three diverse government-industry-university organizations within the designated material synthesis group. These groups then act more or less as one organization to chart the development efforts of FGM materials. These group efforts reflects a policy of the Ministry of Education, Science and Culture ((MESC) where 3-4% of the funded research grants to universities, which are for team projects, receive 43% of the research dollars[1] . Non group projects are under funded and have little chance for long term support.

This method of national project management stresses the use of planning groups of scientists from the diverse organizations to chart the direction of each phase of the development effort. This tactic encourages the growth of specialty research centers at universities such as Professor Hirai's CVD-FGM studies at the High Temperature Material Science Institute at Tohoku University, Professor Watanabe's powder metallurgy FGM studies at Tohoku University, Professor Hiraki's Diamond development studies at the Hiraki Laboratories of Osaka University, and Professor Komiyama' CVD-Semiconductor studies at Tokyo University. The successful centers with high quality research, and the ability to bring attention to their successes, are supported and grow. These centers have a strong voice in national research policy. Research workers from these laboratories carry the university's reputation with them and can find support to continue their research efforts elsewhere. The system discourages research excursions into technologies which are alien to the centers specialty. Organizations with personnel who have no prior experience have a difficult time beginning new research projects.

The National effort for development of Functional Gradient Materials is an example of the Japanese approach. Dr. Masayuki Niino of the National Aerospace Laboratories was the first to draw national attention to gradient materials in Japan in 1984, calling them functionally gradient materials. The Science and Technology Agency of the Japanese Government sponsored a feasibility study on FGM in 1986. Other scientists in Japan such as Professor R. Watanabe of Tohohu University, whose studies may have predated those of Dr. Niino, were also studying gradient materials.

The Japanese Government set up a committee of scientists to plan a national FGM effort. The committee had representatives from government, industry, and universities. The committee recommended the formation of four development groups which would feed information to a Data Base group. The four development groups were: 1. Material Design, 2. Material Synthesis, 3. Testing and Evaluation and 4. Element Testing and Processing. Each development group interfaced directly with the other development groups and supplied information directly to the data based group. Phase I Development studies began in 1987 with government sponsorship of 17 organizations. A successful Phase I effort was followed by a Phase II effort in 1990. An objective of this Phase II effort was to demonstrate the feasibility of fabricating a prototypical National Space Plane 30X30 cm panel made with FGM interface between C/SiC and SiC/SiC components. The Phase II effort ended in March of 1992. A committee of 30 scientists was

selected to plan the new FGM effort. The new FGM program will also examine the utilization of these materials in direct energy conversion systems. This work has now started in Japan with 32 organizations participating in the development effort. Commercialization of these materials is expected to begin in 1998.

The Japanese system promotes high quality efficient use of research dollars. The systematic inclusion of application directed planning into the material development minimizes the time required for commercialization of the technology. The system discourages individual innovation but provides a loophole. Research projects are fully funded by the government, partially funded by the government, or fully funded by the university or company. Projects fully funded by a university or company escape the scrutiny of the national committees but are subjected to the scrutiny of the university or company committees. Thus individual innovation can sometimes succeed. Thus while visually the universities show old and sometimes decaying facilities, successful research projects have sophisticated and expensive experimental hardware. Facilities and research funding at private companies is more difficult to assess. Those shown were obviously well funded. The facilities and experimental hardware used in industrial laboratories were modern, sophisticated, and expensive. This reflects a policy of the major Japanese corporations of investing a larger fraction of corporate funding into research and development. According to M. Kenward[2], the ratio of research money to stockholders dividends for the top 10 R&D corporate spenders was 9.5 in Japan. By contrast, it was 0.70 in Great Britain in 1991. While no similar data was given for spending for R&D by corporations in the United States, it is nearer to that of Great Britain than that of Japan.

2. INTRODUCTION

The ever present desire for product improvement is the driving force behind the need for materials with better mechanical, thermal, electrical, and optical properties. The improved properties of these new materials are obtained by controlling the microstructure of the materials, often on a nanoscale. Two such materials are Functionally Gradient Materials (FGM) and vapor deposited diamond. This report is an assessment of the status of the efforts to develop these technologies at selected sites in Japan. It is recognized that the site choices only represent a fraction of the Japanese activities and may present a skewed view of the total Japanese FGM and diamond research efforts. It is also acknowledged that our site visits only provide a restricted view of the what each organization was willing to discuss about their activities. In spite of these limitations, the site visits did provide an overview of the general goals of these studies and the approaches being taken to meet these goals. To aid in this technical assessment we also drew upon information from published literature, recent technical conferences and personal communications with Japanese research workers to supplement our perspectives from site visits.

3. FUNCTIONALLY GRADIENT MATERIALS

Functionally Gradient Materials differ from other materials by having one or more of the following characteristics: 1. A variable chemical composition, 2. A variable microstructure, 3. A variable density, 4. Variable forms of the same material. One

purpose of these structures is to provide a smooth transition between materials which are otherwise incompatible because of their mechanical or chemical properties. Another purpose is as a coating to modify the electrical, thermal, chemical or optical properties of the substrate upon which the FGM is applied. Gradient materials have historically been used throughout the world to solve difficult problems in joining materials differing in coefficients of thermal expansion (CTE). This differential CTE is particularly troublesome when the materials must be joined at elevated temperatures or must be used at elevated temperatures. Glass-to-metal and quartz-to-metal seals are examples where gradient joints were in use more than forty years ago. By gradually changing the glass composition at the glass-metal joint a seal could be formed which would survive the hot forming process. This process was later used in the 1960's to form high temperature ceramic-to-metal seals [3,4]. A gradient cermet layer with a high metal content on the metal side and a high ceramic content on the ceramic side overcame the problems of CTE mismatch in these ceramic-to-metal seals. Gradient studies continued in the United States but in isolated research efforts[5,6].

The Japanese began a revival of the world's interest in gradient materials in 1987 with a national project called "Research on the Basic Technology for the Development of Functionally Gradient Materials (FGM) for Relaxation of Thermal Stress". These studies were deemed a success when completed in 1991. The name of the national project was expanded and renamed " Feasibility Study of R&D of FGMs as Functional Energy Conversion Materials". Phase I of this work is scheduled for 1993-1995 Phase II, 1996-1997, and Application, 1998-.

FGM are now being evaluated to solve more than just CTE mismatch problems. They are being evaluated as a means of altering the mechanical, thermal, acoustic, electrical, or optical properties of composite materials. Altering these materials properties requires changing the chemical composition, microstructure, state, distribution pattern or other factors in the FGM layer interface between materials. These changes can take place over a relatively short distance, or over the entire length of the component being fabricated.

3.1 Functionally Gradient Materials Research Sites

Table 1. contains information about facilities doing FGM research that we visited from May 24-28, 1993. These selected sites were a mix of government, private companies, and universities laboratories. The senior person in each of these organizations has an international reputation for excellence in his field of study. Observations and brief comments about the technical activities at each site are presented in paragraphs that follow.

Table 1. Functional Graded (FGM) Materials Research Sites Visited

Scientists	Interest	Organization	Location
T. Hirai, M. Omori	FGM, Nano-Composites, CVD, PECVD, ECR-PECVD Superconductors, CVI	Institute For Materials Research Tohoku University	Katahira, Aoba-Ku, Sendai 980
R. Watanabe	FGM with active cooling, SiC-AlN, Ceramic Powders, SiC-AlN/Mo	Dept. Materials Processing, Tohoku University	Sendai, 980
M. Niino, A. Kumakawa, L. Chen, Y. Kuroda, T. Saito	FGM with active cooling, C/C Spaceplane Combustors	Kakuda Research Center National Aerospace Laboratory,	Koganezawa 1, Kimigaya, Kakuda City Miyagi 981-15
J. Fujioka, Y. Matsuzaki, S. Tanaka, T. Suemitsu, K. Hasegawa, M. Kawamura	C/C Spaceplane Combustors, SS/FGM-ZrO_2/SS	Akashi Technical Institute, Kawasaki Heavy Industries, Ltd.	1-1, Kawasaki-cho, Akashi 673, Japan

3.2 Functionally Gradient Assessment Site Observations

3.2.1 Universities

Dr. Toshio Hirai
Institute For Materials Research
Tohoku University
Katahira, Aoba-Ku,
Sendai 980, Japan

Professor Hirai has been experimenting with, and publishing reports about, CVD research internationally for over 25 years. He and his staff are now applying this expertise to FGM research. They are also developing powdered processes for forming these materials. His staff includes an associate professor, 4 research associates, 3 visiting researchers, one technician, and 11 graduate students. They are actively engaged in research on functionally graded materials, nanocomposites, sintering, superconductivity, plasma processing, and solid state ionics. He along with Drs M. Niino and R. Watanabe were on the organizing committees for both the First and Second International Symposiums on Functionally Gradient Materials.

The research activities of he and his staff include:

1. The preparation of FGM by CVD and plasma sintering processes;
2. Corrosion behavior of CVD-FGM TiC/SiC films on steels; and
3. Properties of SiC/C, TiC/C, and HfO_2/SiC/TiC FGM composites.

A significant achievement by Professor Hirai's group has been the development of processes to make 45-130 nm ß-SiC powders. These powders were prepared by a CVD process. By adjusting the process parameters they are able control the particle size, porosity, and chemical composition of these particles. They were also able to produce hollow spheres as well as SiC coated Si microspheres.

Professor Hirai's laboratory is well equipped to form materials by a variety of processes, and to examine them. One particularly impressive piece of hardware was a plasma enhanced hot press.

Dr. Ryuzo Watanabe
Professor, Powder Process Technology,
Dept. Materials Processing,
Faculty of Engineering,
Tohoku University
Sendai 980, Japan

Professor Watanabe of Tohoku University is another of the pioneers of Japanese gradient materials research. He is a prolific publisher of FGM research papers. We are aware of 28 papers, that he and his staff have published, during the period 1986-1992. They have been successful in relating the results of their experimental evaluations of simple geometry FGM specimens to their mechanical property models. They demonstrated this with evaluations of ceramic-to-metal joints in a bumer heating tests. The joints were formed with a graded composition interface between partially stabilized zirconia (PSZ) and 304 stainless steel. Many of these samples are fabricated by a powder spraying process he developed. Three different combinations of FGM layer thicknesses were used in these trials. The results showed they could prevent large crack formation in samples with uniform layer thicknesses, by decreasing the layer thicknesses as one alters the composition from stainless steel to PSZ.

Professor Watanabe does not believe these results can be globally extrapolated to real world, complex geometry components. He speculates that each new FGM material and geometric configuration will require both an analysis of stresses and an experimental examination of process parameters.

3.2.2 National Laboratory

Dr. Masayuki Niino
Chief, Rocket High Altitude
Performance Section,
Kakuda Research Center
National Aerospace Laboratory,
Koganezawa 1, Kimigaya, Kakuda City
Miyagi 981-15, Japan

Dr. Niino, at the National Aerospace Laboratory, is credited with coining the name, Functionally Gradient Materials (FGM), in 1987 and starting the current Japanese National effort on FGM. He is still one of its principle planners. of the National Japanese program on functionally gradient materials (FGM). His group has examined the fabrication of a FGM high pressure thrust chamber by cold isostatic pressing (CIP) Cu-Sn and OFHC Cu. They have also evaluated ZrO_2/Ni FGM barrier coatings for resistance to oxidation and to NO_3/monomethyl hydrazine (NTO)/(MMH) corrosion of the chamber material for regeneratively cooled thrust engine applications.

Dr. Niino and his group are now beginning their evaluation of FGM for energy conversion systems. The system they are evaluating will have: 1. a nuclear heat source, 2. a thermoelectric heat exchanger, with the hot end 2000 K, 3. a thermionic converter, with the hot end 1100 K, 4. a thermoelectric converter, with the hot end 300 K, and 5. heat pipes and a heat rejection system.

3.2.3 Private Company

Dr. Junzoh Fujioka
Senior Manager,
Material Research Department,
Akashi Technical Institute,
Kawasaki Heavy Industries, Ltd.
1-1, Kawasaki-cho,
Akashi 673, Japan

The Akashi Technical Institute is one of four centers at Kawasaki Heavy Industries with research departments. The Institute is housed in 25 buildings, two of which ar over 4 stories high. There are 7 research departments at the Akashi Technical Institute. Material Research is one of these departments. Dr Fujioka and his staff of the Material Research Department are part of the Government-University-Private Industry joint effort to develop FGM technology. The size of his effort is unknown but we met 7 people working on various aspect of FGM research. Their facilities were first class and they appeared to be well funded. The objective Dr. Fujioka's new projects will be the application of FGM to space power systems. The focus of most of his current FGM projects has been the development of materials for the Japanese aerospace plane. His group has examined $MoSi_2$-SiC/TiAl and 3YPSZ/t-TiAl FG thermal barrier coatings for active cooled structures. These FGM materials are prepared by a Gas-Combustion Sintering, Self-propagating High temperature Synthesis (SHS) process at 1400°C. A glass encapsulating process is described which is used to can the material in during high temperature sintering.

Dr. Fujioka'group has also been working on the development of an oxidation resistant, FGM-SiC coating for carbon/carbon composites. Both FGM SiC/C and conventional CVD SiC coatings were evaluated. The CVD SiC coating spalled after one thermal cycle to 2000 K. The comparable FGM coated sample showed no damage even after 10 cycles to 2000 K. All coatings were better than no coating.

4. VAPOR DEPOSITED DIAMOND TECHNOLOGY

Diamond is the hardest material known. It is also more chemically inert, and has a higher thermal conductivity than any known material. It is also unique in being both a good heat conductor and a poor electrical conductor. It is potentially a good high temperature semiconductor with estimated figures of merit of more than 32 times that of silicon, the present day semiconductor standard. P-type diamond occurs in nature from boron impurities. Studies to develop n-type diamond are in progress in Japan, Europe and in the United States. What has limited the development of products which take advantage of the unique properties of diamond has been the lack of suitable fabrication techniques to fabricate diamond in forms applicable to commercialization of this material.

In the late 1950's Spitsyn and Derjaguin in the Soviet Union[7] and early 1960's

Eversole[8] in the United States demonstrated the feasibility of vapor depositing diamond by decomposition of hydrocarbons with low pressure, in 600-1000°C processes. Early experiments were efforts to increase the mass of diamond powders through a vapor deposition process. The resulting deposits contained graphitic-carbon and diamond. Except for experimental efforts in the United States by Angus[9] and a largely ignored effort in the Soviet Union, research on the vapor deposition of diamond languished until the 1980 work of Matsumoto et al.[10] in Japan. They showed the importance of activated hydrogen in the vapor deposition of diamond by a hot filament process and launched an explosion of vapor deposited diamond research projects in Japan and the rest of the world. Experimental diamond research in Japan was sponsored by the Ministry of Education, Science and Culture as a subproject, "Material Processing at extreme Conditions or Non-equilibrium States" of their "New Functionality Materials-Design, Preparation and Control" programs.

Active planning for a Japanese national agenda began with the Diamond Technology Research Meeting (DTRM) in January of 1982. This culminated in the formation of the Japan New Diamond Form (JNDF) in July of 1985. JNDF had participants from universities, national research laboratories, private companies, the Ministry of International Trade, and the Industry and Science technology Agency. The purpose of the form was to exchange information between these groups and to seek new industrial applications for diamond. Seminars were held in 1986 and 1987 within which 39 and 51 presentations respectively were given. The first international seminar was held in Tokyo in 1988. The Second International Conference was held in 1990 in Washington DC within which 159 papers were presented at this meeting [11]. The third International Conference was held in May, 1993 in Honolulu within which 177 papers were presented. Other conferences are also presenting diamond research information. The Second International Applied Diamond Conference will be held in August 1993 in Saitama, Japan. The fourth European Conference on diamond and diamondlike materials will be held in Sept 1993, in Portugal.

4.1 Visited Vapor Deposited Diamond Research Sites

This report attempts to assess the current status of vapor deposited diamond technology in Japan. Just as it was for FGM technology, it was recognized that the organizations we were able to visit represent only a small fraction of the total research facilities involved in vapor deposited diamond research. We again drew upon information from published literature, recent technical conferences and personal communications to aid in this technical assessment and to supplement our historical perspective. Table 2. contains information about facilities doing vapor deposited diamond research that we visited from May 24-28, 1993. Just as those selected for FGM research, these selected sites were a mix of government, private companies, and universities laboratories. Again the senior person in each of these organizations has an international reputation for excellence in his field of study. Observations and brief comments about the technical activities at each site are presented in paragraphs that follow.

Table 2. Vapor Deposited Diamond Research Sites Visited

Scientists	Interest	Organization	Location
A. Hiraki, A. Hatta,	Magneto-Active PECVD, Low Temp. Diamond Semiconductors	Department of Electrical Engineering, Osaka University	2-1, Yamadaoka, Suita-shi Osaka 565
N. Fujimori	Speaker Domes Heat Sinks FET	Itami Research Laboratories, Sumitomo Electric Ind.	1-1-1, Koya-kita, Itami, 664
N. Shohata, K. Baba	Electronics, Optical Windows, X-ray Masks	NEC Corp., Materials Research Laboratory	Miyamae-ku, Kawasaki, Kanagawa 216
T. Inuzuka	Fundamentals of Diamond Growth, Heteroepitaxial Diamond	Aoyama Gakuin University, Electrical Engineering and Electronics	Setagaya-ku Chitosedai 6-16-1 Tokyo 157
K. Nogi	Diamond Nucleation, Joining Ceram./Ceram., Metal/metal, Wetability	Welding Research Institute	11-1 Mihogaoka Ibaraki, Osaka, 567

4.2 Diamond Deposition Assessment Site Observations

4.2.1 Universities

Professor Akio Hiraki
Department of Electrical Engineering
Faculty of Engineering
Osaka University
2-1, Yamadaoka, Suita-shi
Osaka 565, Japan

Professor Hiraki and his staff of the department of Electrical Engineering at Osaka University are involved in a wide spectrum of diamond research projects. His laboratories were well equipped with sophisticated deposition hardware and diagnostic tools. He has chosen to deposit diamond primarily in magnetoreactive microwave plasma systems. He has five of these systems. The advantages of the magnetoreactive system are: 1. It can operate at low pressure where the gas temperature is much lower than the electron temperature. This lowers the diamond etch rate in H°since the etch rate in H° is proportional to temperature. 2. The magnetic field decreases the degrees of freedom for the plasma and allows the absorption of higher power. 3. The plasma fills the chamber more uniformly at low pressure than at high pressure.

Professor Hiraki's group gave five presentations at the recent Third International Symposium on Diamond Materials, held in Honolulu, May 17-21, 1993. His group is attempting to control and decrease the grain size in vapor deposited diamond. They have been able to deposit diamond with 4-5 nm grains by depositing diamond on an ethylene glycol cooled substrate in a magnetoreactive deposition system from methanol and helium.

The objective of a related project was to determine the effect of O_2 in the precursor on the O_2 content in the deposit. They found the H/C ratio in their diamond deposits were proportional to the O_2/C ratio in their precursor. Oxygen 1μm below the surface of their samples could not be removed even with a bombardment with atomic hydrogen. Even a post deposition, 3 min, oxygen exposure at 500°C put 0.32 atom % oxygen in the diamond deposits.

Dr. Hiraki and the staff are aware of world wide important vapor deposited diamond developments. He is not only one of the main organizers of vapor deposited diamond conferences and workshops in Japan but also international symposium on both diamond and semiconductor research.

Dr. Tadao Inuzuka
Professor, Department of
Electrical Engineering and Electronics,
Aoyama Gakuin University

Setagaya-ku Chitosedai 6-16-1
Tokyo 157, Japan

Professor Inuzuka is examining the deposition of diamond by both a DC plasma modification of an electron-assisted, hot-filament CVD process. He showed in 1985 that biasing the substrate during hot-filament diamond deposition improved the deposition rate and film uniformity. These films however contained amorphous carbon and hydrocarbons.

To improve the quality of his diamond films Professor Inuzuka eliminated the hot filament and grew diamond from a DC plasma. He used a Langmiur probe to determine the most favorable processing conditions to grow diamond by monitoring the I-V characteristics of his DC plasma system. Measurements made at 50 torr of a 1% CH_4/H_2 gas mixture plasma were classical with most of the electrical fall potential occurring in the cathode sheath. When the pressure was raised to 200 torr, the potential drop was nearly linear as a function of distance from the anode. An emission spectrometer was used to estimate gas temperatures in the plasma. The estimated gas temperature was 4800-5000°C on the anode side of the plasma in the 200 torr trials and 1000-1500°C in the 50 torr plasma. Almost no diamond deposited in the 50 torr trials while a uniform diamond film was deposited at 200 torr. Deposition rates in these DC plasma systems were up to 10 X as fast as those by the traditional hot-filament process.

He is now operating his DC plasma system at 180 torr. The objective of his current studies is to examine epitaxial diamond growth on foreign substrates by this high rate deposition process. He has recently examined diamond growth on (100), $(111)_N$, and $(111)_B$ surfaces of CBN. Epitaxial diamond grew on (100) cBN. Small, 10 nm epitaxial particles grew and coalesced first into islands and then into a continuous 1-2 μm thick film. Diamond nucleated and grew into continuous 200-300 nm thick films on $(111)_B$ but in 2-3 nm growth steps. Diamond was poorly nucleated on $(111)_N$ CBN.

4.2.2 National Laboratory

Dr. Kiyoshi Nogi
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The Japanese government established the Welding Research Institute at Osaka University in 1969 to promote welding technology. The charter of research at the institute has broadened since 1969 to include all aspects of the material science of joining including, metal and ceramic composites, coatings, properties of materials, and surface modification studies. Dr. Nogi of the Welding Institute is a specialist in surface studies. He has shown that wetability is a good measure of surface properties. He is evaluating solutions to CVD diamond-substrate interface problems. As part of this effort he is attempting to correlate wetability with differences in the deposition behavior of diamond grown on different diamond surfaces. Dr. Nogi recently examined the wetability of diamond by liquid Bi, Pb, Sn, and Ag metals from 1273-1423 K under various reduced pressures. He showed in these experiments that at 200-300°C, the (100) diamond surface is easy and the (111) surface is difficult to wet. Above 1000°C the reverse is true, the (100) surface is hard to wet and the (111) surface is easy to wet. Diamond wetability was modified by adsorbed hydrogen and the presence of carbon. He believes these results will correlate with nucleation and CVD-diamond growth.

4.2.3 Private Companies

Dr. Nobuaki Shohata
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Experimentally Dr. Shohata's group is conducting fundamental research in the deposition of diamond on large area substrates by a hot multi-filament CVD process. The objective of his electron assisted hot-filament studies is to generate uniform, thick, diamond films on large area silicon substrates. The goal is to evaluate diamond coated silicon for heat sink and optical window applications. They are examining nucleation and the beginnings of diamond growth. With this and other information they are trying correlate changes in thermal conductivity and optical properties, with process parameters, of diamond deposits made from methane and hydrogen. Their results thus far have shown that diamond powder pretreatments of silicon wafer surfaces, when carefully done, leaves diamond particles the order of $10^{11}/cm^2$. When

these particles are less than a few tens of nanometers in diameter, they act as nucleation sites for diamond growth. They found both the thermal conductivity and hydrogen contents of these diamond films were sensitive to the CH_4 concentration of the precursor gases. Increasing the methane concentration from 1-3% decreased the thermal conductivity from 1100 W/m-K to 200 W/m-K. This was associated with a 4 fold increase in the hydrogen content of the film.

Dr. Shohata group has also been successful in finding new applications for CVD Diamond technology to meet real world material problems.

Naoji Fujimori
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Naoji Fujimori of the Electronics Materials R&D Department of Sumitomo Electric Industries has been successful in conducting fundamental research and in finding new applications for CVD Diamond technology. It is difficult to assess the total effort expended at Sumitomo on diamond research but the names of 11 professionals appear as coauthors on 8 research papers published by Mr. Fujimori and others at Sumitomo in the past three years.

His group has been consistent in using the latest diamond technology to improve a current commercial product. As early as 1987 they developed a diamond coated alumina speaker diaphragm for tweeters. The diamond coating improved the speaker response from 35 kHz to 50 kHz. They improved upon this in 1990 with a 30 µm thick, free standing diamond speaker diaphragm, having a frequency response of 80 kHz. In a related work they made a surface wave acoustic filter using a ZnO/diamond/Si structure.

Mr. Fujimori's group successfully boron doped diamond to make a P-type diamond semiconductor. They then used this process to form a thermistor which would operate from R.T. to 600°C. Using boron-doped epitaxial diamond films, they also successfully made an Field-Effect Transistor (FET) and a light emitting diode. Their most successful application of vapor deposited diamond technology has been the development of diamond coated tape automated bonding (TAB) tools used in the manufacture of electronic packaging. These diamond coated tools are flatter, have higher wear resistance, have 2-3 times the tool life, and are expected to have 1/3 the production cost of traditional, sintered, polycrystalline diamond.

5. DISCUSSION

This report attempts to assess the current status of FGM and Vapor Deposited Diamond technologies in Japan from selected site visits and supplemental information. It is recognized that the organizations we were able to visit represented only a small fraction of the total research facilities involved in these developments. However, the supplemental information from open literature reports and discussions with Japanese scientists from other organizations, reenforced the view that the sites visited in this assessment study gave an appropriate overview of the overall status of these technologies in Japan.

The Japanese are world leaders in both vapor deposited diamond technology and functionally gradient materials. The credit for this success, to a large measure, is rooted in Japanese culture and their tradition of team efforts. The Japanese government places new product research high on its list of national priorities. It encourages team projects in research as a way of maintaining Japan's competitive edge. The Ministry of Education, Science and Culture (MESC) of the Japanese Government through its emphasis on grant money for team projects, has a strong influence on what national research and development projects are funded, even by private companies. It promotes the formation of research teams. University, government and private industrial laboratories are included in these research team. Each member has a defined roll in the projects and duplications of research efforts are minimal. Functionally Gradient Materials technology is one of these national team projects. In its present stage of development there is strong government involvement. When a national effort has matured and commercialization is feasible, government involvement is reduced and private industry bears most of the cost of further technology improvements. Vapor deposited diamond is nearing this stage of development.

5.1 Functionally Gradient Materials Technology

The Japanese are making rapid progress in basic experimental FGM studies, analytical modeling and application oriented FGM developments. Gradient materials have been used for years in the United States to solve differences in CTE's between materials in joints and coatings. These American efforts were sporadic and largely used to solve peripheral problems of larger application research projects. The current Japanese effort considers FGM as a separate class of materials and as such is exploring the limits of these materials beyond those of simply being interface materials. Thirty two government, university, and private company laboratories are participating in a new, national, Functionally Gradient Materials research effort.

With this emphasis on gradient materials as a separate class of materials, the Japanese are making rapid progress toward the commercialization of FGM. They are currently applying techniques for fabricating these materials to metallic and non metallic composite structures. The purpose of these structures is to extend the operating limits of materials exposed to severe environments of heat, abrasive, and corrosion. They are developing new materials with directionally controlled properties for direct power conversion, and electronic applications. They are seeking new applications for FGM technologies. Large Japanese corporations are sponsoring long term FGM research projects in their own laboratories and expect to have profitable commercial FGM products in 5 years.

5.2 Vapor Deposited Diamond Technology

This was the second time an assessment of Vapor deposition of Diamond research in Japan was made by the authors. The first was in 1988 after visits to 6 universities and 4 national laboratories engaged in diamond research. The number of deposition methods used by Japanese laboratories to deposit diamond has not changed appreciably in the past five years. However, both the experimental equipment and the process procedures used to control these deposition processes are now much more complex. The difference is due to the current awareness of the experimental sophistication required to produce viable diamond products. Most deposits made in 1988 were mixtures of diamond and graphite. Diamond was nonuniformly deposited and its adhesion on foreign substrates was poor. While not optimized, solutions to many of these problems have been found.

In spite of the extensive international effort, many problems must be solved before the commercialization of diamond is a reality. Universities, industrial and government laboratories continue to make advances in vapor deposited diamond research. The Japanese have improved their basic understanding of what controls diamond growth and how to minimize carbon contamination. Many of the problems are related to the fact that diamond is metastable with respect to graphite at the temperatures and low pressures it is formed in current vapor deposition processes. Thermodynamic and kinetic issues during diamond formation are still being resolved and are at the root of Japanese basic research projects. They are beginning to understand what controls nucleation in CVD diamond process. They have improved the area, thickness, and uniformity of diamond films they are depositing. Methods of controlling the nucleation of diamond on foreign surfaces are also being sought in these research efforts.

There is no apparent difference between the level of sophistication and the progress being made in basic diamond research in Japan from that being done in the United States and Europe. The Japanese however, have a clear edge in their progress toward the commercialization of diamond deposition processes. Most of the commercial diamond processes in the United States are being done by small private companies with limited financial resources. By contrast, large Japanese industrial conglomerates are supporting long term application oriented diamond deposition research projects. Many demonstration products have already been made but are not yet economically competitive with non vapor deposited products.

6. RECOMMENDATIONS

6.1 The Japanese do not begin new efforts on spur of the moment decisions. Teams are formed for long range research planning. Team members originate from participants at local and international research symposia and conferences. American participation in these conferences necessary if we are to stay current with Japanese planning.

6.2 American participants in foreign international conferences should not only rely on private industry but should receive government financial support for their participation.

6.3 Interfacial meetings between American scientists should not be through infrequent visits by large groups. The larger the groups, the more formal are the meetings and the more guarded is the information passed between the groups.

6.4 Sponsorship of American graduate and postdoctoral students to Japanese universities should receive United States government support. This would provide a long term exchange of ideas between our two countries.

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